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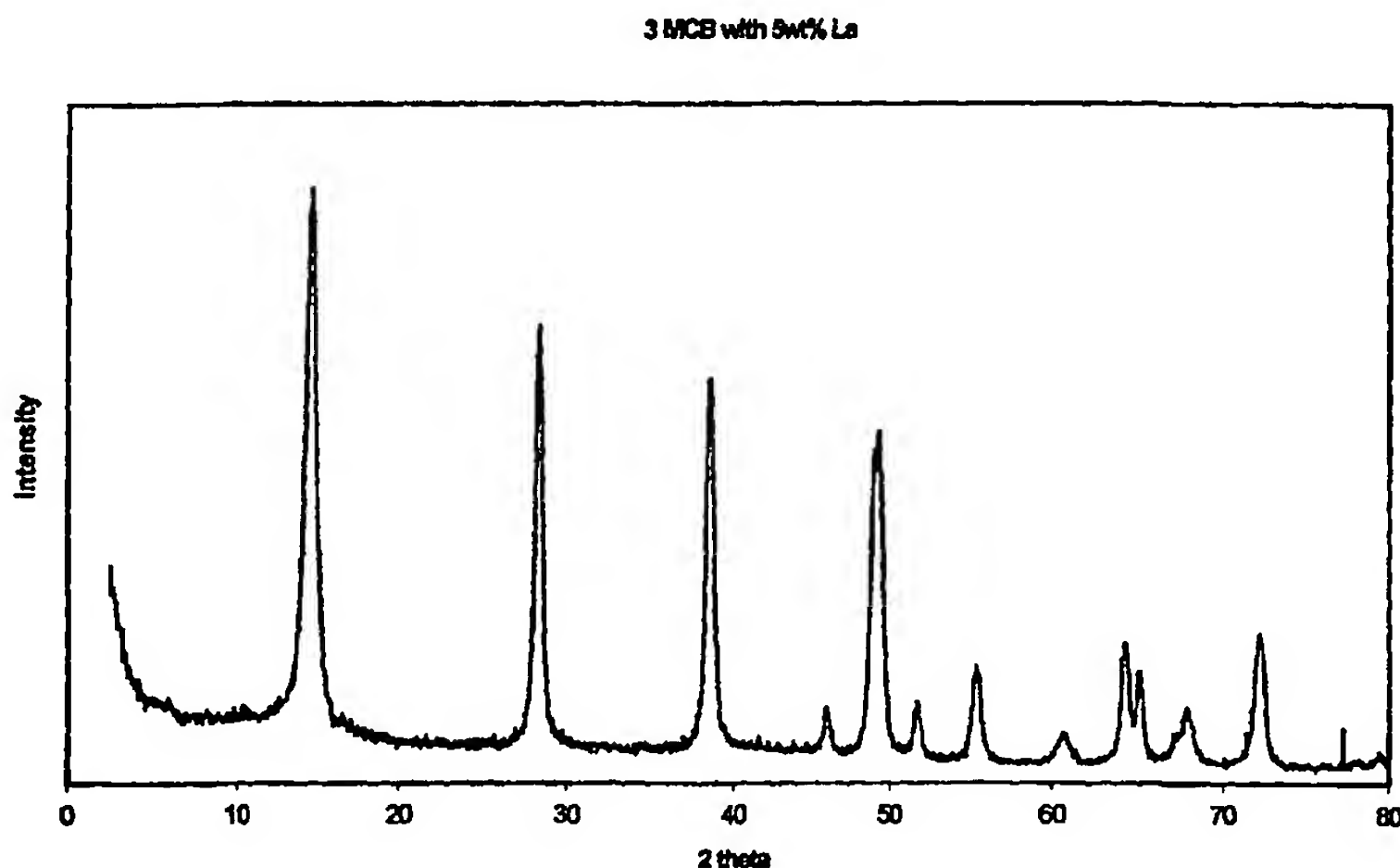
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(54) Title: MICRO-CRYSTALLINE BOEHMITES CONTAINING ADDITIVES AND SHAPED PARTICLES AND CATALYST COMPOSITIONS COMPRISING SUCH MICRO-CRYSTALLINE BOEHMITE



(57) Abstract: The present invention pertains to a micro-crystalline boehmite containing additive in a homogeneously dispersed state. Suitable additives are compounds containing elements selected from the group of alkaline earth metals, alkaline metals, rare earth metals, transition metals, actinides, silicon, gallium, boron, titanium, and phosphorus. Said MCBs according to the invention may be prepared in several ways. In general, a micro-crystalline boehmite precursor and an additive are converted to a micro-crystalline boehmite containing the additive in a homogeneously dispersed state. Also claimed are shaped particles and catalyst compositions comprising the as-prepared micro-crystalline boehmite.

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MICRO-CRYSTALLINE BOEHMITES CONTAINING ADDITIVES AND SHAPED PARTICLES AND  
CATALYST COMPOSITIONS COMPRISING SUCH MICRO-CRYSTALLINE BOEHMITE

5 The present invention pertains to micro-crystalline boehmites containing  
additives. Alumina, alpha-monohydrates or boehmites and their dehydrated  
and or sintered forms are some of the most extensively used aluminium oxide-  
hydroxides materials. Some of the major commercial applications, for  
example, ceramics, abrasive materials, fire-retardants, adsorbents, catalysts  
10 fillers in composites, and so on, involve one or more forms of these materials.  
Also, a substantial portion of commercial boehmite aluminas is used in  
catalytic applications such as refinery catalysts, catalyst for hydroprocessing  
hydrocarbon feeds, reforming catalysts, pollution control catalysts, cracking  
catalysts. The term "hydroprocessing" in this context encompasses all  
15 processes in which a hydrocarbon feed is reacted with hydrogen at elevated  
temperature and elevated pressure. These processes include  
hydrodesulphurisation, hydrodenitrogenation, hydrodemetallisation,  
hydrodearomatisation, hydro-isomerisation, hydrodewaxing, hydrocracking,  
and hydrocracking under mild pressure conditions, which is commonly referred  
20 to as mild hydrocracking. This type of alumina is also used as a catalyst for  
specific chemical processes such as ethylene-oxide production and methanol  
synthesis. Relatively more recent commercial uses of boehmite types of  
aluminas or modified forms thereof involve the transformation of  
environmentally unfriendly chemical components such as  
25 chlorofluorohydrocarbons (CFCs) and other undesirable pollutants. Boehmite  
alumina types are further used as catalytic material in the combustion of gas  
turbines for reducing nitrogen oxide.

The main reason for the successful extensive and diversified use of these  
30 materials in such variety of commercial uses is their flexibility, which enables

them to be tailor-made into products with a very wide range of physico-chemical and mechanical properties.

Some of the main properties which determine the suitability of commercial applications involving gas-solid phase interactions such as catalysts and adsorbents are pore volume, pore size distribution, pore texture, specific density, surface areas, density and type of active centre, basicity and acidity, crushing strength, abrasion properties, thermal and hydrothermal aging (sintering), and long-term stability.

10

By and large, the desired properties of the alumina product can be obtained by selecting and carefully controlling certain parameters. These usually involve: raw materials, impurities, precipitation or conversion process conditions, aging conditions and subsequent thermal treatments (calcinations/steamings), and mechanical treatments.

15

Nevertheless, in spite of this wide and diversified range of existing know-how, this technology is still under development and presents unlimited scientific and technological challenges to both the manufacturers and the end-users for further development of such alumina-based materials.

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The term boehmite is used in the industry to describe alumina hydrates which exhibit XRD patterns close to that of aluminium oxide-hydroxide  $[\text{AlO}(\text{OH})]$ , naturally occurring boehmite or diaspore. Further, the general term boehmite tends to be used to describe a wide range of alumina hydrates which contain different amounts of water of hydration, have different surface areas, pore volumes, and specific densities, and exhibit different thermal characteristics upon thermal treatment. Yet although their XRD patterns exhibit the characteristic boehmite  $[\text{AlO}(\text{OH})]$  peaks, their widths usually vary and they can also shift location. The sharpness of the XRD peaks and their locations

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30

have been used to indicate the degree of crystallinity, crystal size, and amount of imperfections.

Broadly, there are two categories of boehmite aluminas. Category I, in  
5 general, contains boehmites which have been synthesised and/or aged at  
temperatures close to 100°C, most of the time under ambient atmospheric  
pressure. This type of boehmite is referred to as quasi-crystalline boehmite.  
The second category of boehmites which is the subject of the present  
invention consists of so-called micro-crystalline boehmites.

10

In the state of the art, category I boehmites, i.e. quasi-crystalline boehmites,  
are referred to interchangeably as: pseudo-boehmites, gelatinous boehmites  
or quasi-crystalline boehmites (QCBs). Usually, these QCB aluminas have  
very high surface areas, large pores and pore volumes, and lower specific  
15 densities than microcrystalline boehmites. They disperse easily in water of  
acids, have smaller crystal sizes than micro-crystalline boehmites, and contain  
a larger number of water molecules of hydration. The extent of hydration of the  
QCB can have a wide range of values, for example from about 1.4 up, and  
about 2 moles of water per mole of AlO, usually intercalated orderly or  
20 otherwise between the octahedral layers.

The DTG (differential thermogravimetry) curves of the water release from the  
QCB materials as a function of temperature show that the major peak appears  
at much lower temperatures compared to that of the much more crystalline  
boehmites.

25 The XRD patterns of QCBs show quite broad peaks, and their half-widths are  
indicative of the crystal size as well as the degree of crystal perfection.

The broadening of the widths at half-maximum intensities varies substantially  
and for the QCBs typically can be from about 2° - 6° to 2θ. Further, as the  
30 amount of water intercalated in the QCB crystals is increased, the main (020)

XRD reflection moves to lower  $2\theta$  values corresponding to greater d-spacings. Some typical, commercially available QCB's are: Condea Pural ®, Catapal ® and Versal ® products.

5 The category II boehmites consist of microcrystalline boehmites (MCBs), which are distinguished from the QCBs by their high degree of crystallinity, relatively large crystal sizes, very low surface areas, and high densities. Unlike the QCBs, the MCBs show XRD patterns with higher peak intensities and very narrow half-peak line widths. This is due to the relatively small number of  
10 intercalated water molecules, large crystal sizes, higher degree of crystallisation of the bulk material, and smaller amount of crystal imperfections present. Typically, the number of intercalated molecules of water can vary from about 1 up to about 1.4 per mole of AlO. The main XRD reflection peaks (020) at half-length of maximum intensity have widths from about 1.5 down to  
15 about 0.1 degree 2-theta ( $2\theta$ ). For the purpose of this specification we define micro-crystalline boehmites as having 020 peak widths at half-length of the maximum intensity of smaller than 1.5 °. Boehmites having a 020 peak width at half-length of maximum intensity larger than 1.5 are considered quasi-crystalline boehmites.

20

A typical commercially available MCB product is Condea's P-200 ® grade of alumina. Overall, the basic, characteristic differences between the QCB and MCB types of boehmites involve variations in the following: 3-dimensional lattice order, sizes of the crystallites, amount of water intercalated between the  
25 octahedral layers, and degree of crystal imperfections.

As for the commercial preparation of these boehmite aluminas, QCBs are most commonly manufactured via processes involving:

Neutralisation of aluminium salts by alkalines, acidification of aluminate salts,  
30 hydrolysis of aluminium alkoxides, reaction of aluminium metal (amalgamated)

with water, and rehydration of amorphous rho-alumina obtained by calcining gibbsite. The MCB types of boehmite aluminas in general are commercially produced by hydrothermal processes using temperatures usually above 150°C and autogeneous pressures. These processes usually involve hydrolysis of aluminium salts to form gelatinous aluminas, which are subsequently hydrothermally aged in an autoclave at elevated temperatures and pressures. This type of process is described in US 3,357,791. There are several variations on this basic process involving different starting aluminium sources, additions of acids or salts during the aging, and a wide range of process conditions.

MCBs are also prepared using hydrothermal processing of gibbsite or thermally treated forms of gibbsite. Variations on these processes involve: addition of acids, alkaline metals, and salts during the hydrothermal treatment, as well as the use of boehmite seeds to enhance the conversion of gibbsite to MCB. These types of processes are also described in Alcoa's US 5,194,243, in US 4,117,105.

US 4,797,139 describes the hydrothermal processing of aluminum trihydrate and MCB as a seed to form MCB, which can act as a precursor for alpha-alumina ceramic bodies. In order to enhance the conversion of said MCB in alpha-alumina zirconia or zirconium oxide precursor and/or magnesium oxide precursor may be added prior to the reaction in the autoclave.

Nevertheless, whether pseudo-, quasi- or microcrystalline, such boehmite materials are characterised by reflections in their powder X-ray. The ICDD contains entries for boehmite and confirms that there would be reflections corresponding to the (020) , (021), and (041) planes. For copper radiation, such reflections would appear at 14, 28, and 38 degrees 2-theta. The various forms of boehmite would be distinguished by the relative intensity and width of

the reflections. Various authors have considered the exact position of the reflections in terms of the extent of crystallinity. Nevertheless, lines close to the above positions would be indicative of the presence of one or more types of boehmite phases.

5

In the prior art, we find QCBs containing metal ions which have been prepared by hydrolysis of alumina isopropoxide with co-precipitation of lanthanides, as described in the paper by J. Medena, *J. Catalysis*, Vol. 37 (1975), 91-100, and J. Wachowski et al., *Materials Chemistry*, Vol. 37 (1994), 29-38. The products  
10 are pseudo-boehmite type aluminas with the occlusion of one or more lanthanide metal ions. These materials have been used primarily in high-temperature commercial applications where the presence of such lanthanide metal ions in the pseudo-boehmite structure retards the transformation of the gamma-alumina to the alpha-alumina phase. Therefore, a stabilisation of the  
15 gamma phase is obtained, i.e. a higher surface area is maintained before conversion to the refractory lower surface area alpha-alumina. Specifically, Wachowski et al. used the lanthanide ions (La, Ce, Pr, Nd, Sm) in quantities from 1% to 10% by weight, calcined at temperatures in the range of 500°C to 1200°C. No information is provided by Wachowski et al. regarding the state  
20 and properties of the materials below 500°C, which is the most important area for catalytic applications.

Also, EP-A1-0 597 738 describes the thermal stabilisation of alumina by the addition of lanthanum, optionally combined with neodymium. This material is  
25 prepared by aging flash-calcined Gibbsite in a slurry with a lanthanum salt at a temperature between 70 and 110°C, followed by a thermal treatment at a temperature between 100 and 1000°C. The intermediate product, prior to thermal treatment is a QCB.



The final products, like the products produced by Wachowski et al., all are high-temperature refractory (ceramic) materials which because of their bulk structures of extremely high density, very low surface areas, and small pores find very limited application in heterogeneous catalysis, especially for catalysts  
5 used in hydrocarbon conversion or modification, for example FCC and hydroprocessing commercial applications.

Further, EP-A-0 130 835 describes a catalyst comprising a catalytically active metal supported on a lanthanum or neodymium- $\beta$ - $\text{Al}_2\text{O}_3$  carrier. Said carrier is  
10 obtained by the precipitation of aluminium nitrate solution with ammonium hydroxide in the presence of a lanthanum, praseodimium or neodymium salt solution. As the precipitated amorphous material is directly washed with water and filtered, the alumina is not allowed to age with time under the usual conditions and a certain pH, concentration, and temperature, so that it  
15 crystallises to a boehmite alumina structure.

The present invention is directed to micro-crystalline boehmite wherein an additive which improves the MCB's suitability for use in catalytic or absorbent material is present in a homogeneously dispersed state.

20

In the prior art QCBs containing homogeneously dispersed additives are known, e.g. the lanthanide containing intermediate product of the process described in Wachowski. Said additives retard the conversion of gamma-alumina to alpha-alumina which has a very low surface area and is therefore  
25 useless as a catalytic or absorbent material. It was found that MCBs containing said lanthanides in a homogeneously dispersed state have an improved thermal stability over QCBs containing lanthanides. As mentioned-above micro-crystalline boehmites with their high crystallinity, specific surface area etcetera, may be used for specific applications in the catalyst field or  
30 absorbent field.



The additive present in the MCB according to the invention helps to adjust the MCB's physical, chemical, and catalytic properties such as specific density, surface area, thermal stability, pore size distribution, pore volume, density and  
5 type of active centres, basicity and acidity, crushing strength, abrasion properties, etcetera, which determine the boehmite's suitability for use in catalytic or absorbent material. As will be clear from the above, additives which enhance the formation of alpha-alumina such as zirconia and magnesia are not considered additives which improve the MCBs suitability for catalytic and  
10 absorbent material and are therefore not part of the invention. The fact that the additive is homogeneously dispersed within the MCB distinguishes the MCBs according to the invention from MCBs which have been impregnated with additives, and renders these new MCBs extremely suitable for catalytic purposes or as starting materials for the preparation of catalysts for  
15 heterogeneous catalytic reactions. It is easy to determine that an additive is not homogeneously dispersed in the micro-crystalline alumina, because in that case the additive is present as a separate phase and is detectable in the X-ray diffraction pattern. It is, of course, possible to incorporate different types of additives into the MCB according to the invention.

20

Suitable additives are compounds containing elements selected from the group of alkaline earth metals, rare earth metals, alkaline metals, transition metals, actinides, noble metals such as Pd and Pt, silicon, gallium, boron, titanium, zirconium, and phosphorus. For instance, the presence of silicon  
25 increases the amount of acidic sites in the boehmite, transition metals introduce catalytic or absorbing activity such as SO<sub>x</sub> captivation, NO<sub>x</sub> captivation, hydrogenation, hydroconversion, and other catalytic systems for gas/solid interactions.

Suitable compounds containing the desired elements are nitrates, sulphates, chlorides, formates, acetates, carbonates, vanadates, etcetera. The use of compounds with decomposable anions is preferred, because the resulting MCBs with additive can be dried directly, without any washing, as anions  
5 undesirable for catalytic purposes are not present.

Said MCBs according to the invention can be prepared in several ways. In general, a micro-crystalline boehmite precursor and an additive are combined and converted by aging to a micro-crystalline boehmite containing the additive  
10 in a homogeneously dispersed state. Aging can be done thermally or hydrothermally. The aging is done in a protic liquid or gas such as water, ethanol, steam, propanol. Hydrothermal aging means aging under increased pressure for instance, in water in an autoclave at a temperature above 100 °C, i.e. under autogeneous pressure. Suitable micro-crystalline boehmite  
15 precursors are aluminium alkoxides, soluble aluminium salts, thermally treated aluminium trihydrate, aluminium trihydrate such as BOC, Gibbsite and bayerite, amorphous gel alumina, QCBs or MCBs. Examples of suitable preparation processes are described below:

#### 20 Process 1

The MCB can be prepared by hydrolysing and aging an aluminium alkoxide in the presence of a compound containing the desired additive(s). The additive can be incorporated during the hydrolysis step or added at the end before the  
25 aging step. This general process is known for the preparation of QCBs, but when adapted it is possible to prepare MCBs using this process. To this end the process is either conducted at a temperature above 100 °C and at increased pressure or by subjecting the QCB obtained by hydrolysatation at a temperature below 100 °C to a hydrothermal post-aging treatment.

### Process 2

The MCB can be prepared by hydrolysis and precipitation as hydroxides of soluble aluminium salts and aged to form a MCB containing additive.

- 5 Examples of suitable aluminium salts are aluminium sulphate, aluminium nitrate, aluminium chloride, sodium aluminate, and mixtures thereof. The additive(s) may be added while the hydrolysis and coprecipitation are going on or at the end in the aging step. In order to form MCBs either the aging step must be conducted under hydrothermal conditions, or a hydrothermal post-aging step must be applied.
- 10

### Process 3

- The MCB can also be prepared by aging a slurry containing a thermally treated form of aluminium trihydrate and additive(s) at a temperature above
- 15 100 °C at increased pressure, preferably at autogeneous pressure for a time sufficient to form MCBs. Thermally treated forms of aluminium trihydrate are calcined aluminium trihydrate (e.g. Gibbsite or BOC) and flash calcined aluminium trihydrate (CP ® alumina). This preparation method has the
- 20 advantage that no ions are introduced into the MCB apart from any ions present in the additive compound. That means that with the appropriate choice of additive compounds washing steps can be reduced or avoided altogether. For instance, when decomposable anions (such as carbonates, nitrates, and formates) are used, the MCB containing additive can be dried directly, as
- 25 anions undesirable for catalytic purposes are not present. A further advantage of this preparation method is that it is possible to first shape a slurry containing a thermally treated form of aluminium trihydrate and additive, reslurry the shaped bodies, and subsequently age the shaped bodies to form MCBs. Shaping is defined in this specification as any method of obtaining particles
- 30 with the appropriate size and strength for the specific purpose. Suitable

shaping methods are spray-drying, extrusion (optionally with intermediate spray-drying, filterpressing and/or kneading), pelletising, beading or any other conventional shaping method used in the catalyst or absorbent field and combinations thereof.

5

#### Process 4

The MCB can also be prepared by aging a slurry containing amorphous gel alumina and additive(s) at a temperatures above 100 °C at increased pressure to form MCBs, preferably at autogeneous pressure. Like process 3 mentioned above, this preparation method also has the advantage that no ions are introduced into the MCB apart from the ions of the additive compound. This means that with the appropriate choice of additive compounds washing steps can be reduced or avoided altogether. Also, it is possible to first shape a slurry containing amorphous alumina gel and additive, reslurry the shaped bodies, and subsequently age the shaped bodies to form MCBs.

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#### Process 5

MCBs according to the invention can also be prepared by aging QCB or MCB by thermal or hydrothermal treatment in the presence of compounds of the desired additive to form a MCB containing additive in a homogeneously dispersed state. This process also allows shaping of the QCB or MCB/additive mixture before the (hydro)thermal treatment and formation of MCB containing additive in a homogeneously dispersed state. Further, no ions other than the ions of the additive compound are introduced into the MCB.

20

25

#### Process 6

MCBs can also be prepared by aging alumina trihydrates such as gibbsite, BOC, and bayerite by hydrothermal treatment, optionally with the aid of suitable boehmite seeds in the presence of compounds of the desired additives. Suitable seeds are the known seeds to make microcrystalline boehmite such as commercially available boehmite (Catapal ®, Condea  
5 ®Versal, P-200 ®, etcetera), amorphous seeds, milled boehmite seeds, boehmite prepared from sodium aluminate solutions, etcetera. Also microcrystalline boehmites prepared by one of the processes described here can suitably be used as a seed. Like processes 3, 4, and 5 no ions other than the  
10 ions of the additive are introduced into the MCB, and this process allows shaping prior to the aging step.

The first publications on the use of seeds in the hydrothermal conversion of aluminum trihydrate date back in the late 1940's/early 1950's. For example, G.  
15 Yamaguchi and K. Sakamoto (1959), clearly demonstrate the concept that boehmite seeds substantially improved the kinetics of the hydrothermal conversion of gibbsite to boehmite, by lowering the temperature, shorten the reaction time, and increase the gibbsite conversion.

20 Also the beneficial principle of seeding with boehmite in the hydrothermal transformation of gibbsite in an autoclave operating at elevated temperatures and autogeneous pressures was also demonstrated clearly by G. Yamaguchi and H. Yamanida (1963).

25 There are several other publications in the open literature, in which equally well the benefits of seeding with boehmite and/or alkaline solutions are demonstrated. Further, the use of boehmite seed is also claimed to produce finer particle size boehmite product which is easier to disperse in water. The use of boehmite seeds in the hydrothermal conversion of gibbsite has been

described in US 4,797,139, filed on December 16, 1987. and in US 5,194,243, filed on September 30, 1985

All the processes described above may be conducted batch-wise or in a  
5 continuous mode, optionally in a continuous multi-step operation. The processes may also be conducted partly continuous, partly batch-wise.

As mentioned above, more than one type of MCB precursor may be used, although care must be taken that the reaction conditions employed enable the  
10 conversion of the precursor to MCB. Said mixture of MCB precursors may be prepared before introduction of the additive, or the various types of precursors may be added in any of the further stages of the reaction.

In the processes for the preparation of the MCBs according to the invention  
15 more than one aging step may be applied, wherein for instance the aging temperature and/or condition (thermally or hydrothermally, pH, time) is varied.

The reaction products of the processes for the preparation of the MCBs according to the invention may also be recycled to the reactor.

20

If more than one type of additive is incorporated into the MCB, the various additives may be added simultaneously or sequentially in any of the reaction steps.

25 It may be advantageous to add acids or bases to adjust the pH during the hydrolysis, precipitation and/or aging steps.

As mentioned above, some of the processes for the preparation of the micro-crystalline boehmites according to the invention allow shaping into shaped  
30 bodies during preparation. It is also possible to shape the final MCB, optionally

with the help of binders and/or fillers. Suitable shaping methods include spray-drying, pelletising, extrusion (optionally with intermediate spray-drying, filterpressing and/or kneading), beading, or any other conventional shaping method used in the catalyst and adsorbent field or combinations thereof.

5

As mentioned above, the MCBs according to the invention are extremely suitable as components or starting material for catalyst compositions or catalyst additives. To this end the MCB is combined with, optionally, binders, fillers (e.g. clay such as kaolin, titanion oxide zirconia, silica, silica-alumina  
10 bentonite, etcetera), catalytically active material such as molecular sieves (e.g. ZSM-5, zeolite Y, USY zeolite), and any other catalyst components such as for instance pore regulating additives, which are commonly used in catalyst compositions. For some applications it may be useful to neutralise the QCB before use as a catalyst component, for instance to improve or create pore  
15 volume or other important properties, especially if the QCB has been prepared at low pH. Usually it is preferred to remove any sodium to a content of below 0.1 wt% Na<sub>2</sub>O. The present invention therefore is also directed to catalyst compositions and catalyst additives comprising the MCB according to the invention.

20

In a further embodiment of the invention, the MCB may be mixed with other metal oxides or hydroxides, binders, extenders, activators, pore regulating additives etcetera in the course of further processing to produce absorbents, ceramics, refractories, substrates, and other carriers.

25

For catalytic purposes, boehmites are generally used at temperatures between 200 and 1300°C. At these high temperatures the boehmites are usually converted into transition-aluminas. Therefore, the present invention is also directed to transition alumina which is obtainable by thermal treatment of the  
30 micro-crystalline boehmite containing additive according to the invention and



to transition alumina wherein additives are present in a homogeneously dispersed state. The invention is further directed to transition alumina wherein said additives are compounds containing elements selected from the group of alkaline earth metals, transition metals, actinides, silicon, boron, and  
5 phosphorus.

With the above-mentioned transition aluminas catalyst compositions or catalyst additives can be made, optionally with the help of binder materials, fillers, etcetera.

10

The present invention will be further illustrated by means of the following non-limiting examples.

## EXAMPLES

15

### Comparative example 1

An XRD spectrum was made of Catapal A®, ex Vista Chemicals, a quasi-crystalline boehmite. See Figure 1.

### 20 Comparative example 2

An XRD spectrum was made of P200®, ex Condea, a microcrystalline boehmite. See Figure 2.

### 25 Example 3

Catapal® was treated along with 5 wt%  $\text{La}(\text{NO}_3)_3$  (calculated as  $\text{La}_2\text{O}_3$ ) at a pH of 4 for 2 hours at a temperature of 220°C in an autoclave. Figure 3 shows the XRD pattern of the MCB formed.

30

### Example 4

Micral 916 ® Gibbsite was treated with 5 wt%  $\text{La}(\text{NO}_3)_2$  (calculated as  $\text{La}_2\text{O}_3$ ) at a pH of 4 for 2 hours at a temperature of 220°C in an autoclave Example 4. Figure 4 shows the XRD pattern of the MCB formed.

5    Example 5

Micral 916 ® Gibbsite was treated with 5 wt%  $\text{La}(\text{NO}_3)_2$  (calculated as  $\text{La}_2\text{O}_3$ ) at a pH of 11 for 2 hours at a temperature of 220°C in an autoclave.

10   Example 6

Flash calcined Gibbsite was treated with 5 wt%  $\text{La}(\text{NO}_3)_2$  (calculated as  $\text{La}_2\text{O}_3$ ) at a pH of 4 for 2 hours at a temperature of 220°C in an autoclave. Figure 5 shows the XRD pattern of the MCB formed.

15   Example 7

Flash calcined Gibbsite was treated with 5 wt%  $\text{La}(\text{NO}_3)_2$  (calculated as  $\text{La}_2\text{O}_3$ ) at a pH of 11 for 2 hours at temperature of 220°C in an autoclave.

20   Example 8

A sample of bayerite was treated at a pH of 4 with 5 wt%  $\text{La}(\text{NO}_3)_2$  (calculated as  $\text{La}_2\text{O}_3$ ) for 2 hours at a temperature of 220°C in an autoclave. Figure 6 shows the XRD pattern of the MCB formed.

25

Example 9

A mixture of Gibbsite, Catapal and 5 wt%  $\text{La}(\text{NO}_3)_2$  (calculated as  $\text{La}_2\text{O}_3$ ) were treated at a pH of 4 for two hours in an autoclave at 220 °C. Figure 7 shows  
30   the XRD pattern of the MCB formed.

Example 10

A mixture of Gibbsite, Catapal and 5 wt%  $\text{La}(\text{NO}_3)_2$  (calculated as  $\text{La}_2\text{O}_3$ ) were treated at a pH of 11 for two hours in an autoclave at 220 °C.

5

Example 11

A mixture of Gibbsite, CP alumina and 5 wt%  $\text{La}(\text{NO}_3)_2$  (calculated as  $\text{La}_2\text{O}_3$ ) were treated at a pH of 11 for two hours in an autoclave at 220 °C.

10

Example 12

A mixture of Gibbsite, CP alumina and 5 wt%  $\text{La}(\text{NO}_3)_2$  (calculated as  $\text{La}_2\text{O}_3$ ) were treated at a pH of 4 for two hours in an autoclave at 220 °C. Figure 8 shows the XRD pattern of the MCB formed.

15

Example 13

P-200 ® was treated along with 5 wt%  $\text{La}(\text{NO}_3)_2$  (calculated as  $\text{La}_2\text{O}_3$ ) at a pH of 4 for 2 hours at a temperature of 220°C in an autoclave.

20

Example 14

CP alumina ® was treated along with 5 wt%  $\text{Ce}(\text{NO}_3)_3$  (calculated as  $\text{CeO}_3$ ) at a pH of 10 for 1 hour at a temperature of 200°C in an autoclave. Figure 9 shows the XRD pattern of the MCB formed.

25

Example 15

CP alumina ® was treated along with 5 wt% ZnO at a pH of 10 for 1 hour at a temperature of 200°C in an autoclave. Figure 10 shows the XRD pattern of the MCB formed.

5    Example 16

CP alumina ® was treated along with 5 wt% Ba(NO<sub>3</sub>)<sub>2</sub> (calculated as the oxide) at a pH of 9 for 1 hour at a temperature of 200°C in an autoclave. Figure 11 shows the XRD pattern of the MCB formed.

10

Example 17

BOC was treated along with 5 wt% La(NO<sub>3</sub>)<sub>2</sub> (calculated as La<sub>2</sub>O<sub>3</sub>) at a pH of 4 for 1 hour at a temperature of 220°C in an autoclave. Figure 12 shows the XRD pattern of the MCB formed.

15

Example 18

CP alumina ® was treated along with 10 wt% Ga(NO<sub>3</sub>)<sub>3</sub> (calculated as the oxide) at a pH of 6 for 1 hour at a temperature of 200°C in an autoclave. Figure 13 shows the XRD pattern of the MCB formed.

20

Example 19

CP alumina ® was treated along with 5 wt% SiO<sub>2</sub> at a pH of 10 for 1 hour at a temperature of 200°C in an autoclave. Figure 14 shows the XRD pattern of the MCB formed.

25

Example 20

30

Gibbsite and CP alumina ® (RATIO 70:30) was treated along with 5 wt%  $\text{La}(\text{NO}_3)_3$  (calculated as  $\text{La}_2\text{O}_3$ ) at a pH of 10 for 1 hour at a temperature of 200°C in an autoclave. Figure 15 shows the XRD pattern of the MCB formed.

## 5 Example 21

Samples of Catapal ®, P-200 ®, a quasi-crystalline boehmite containing 5 wt% lanthanide in a homogeneously dispersed state and a microcrystalline containing 5 wt% lanthanide in a homogeneously dispersed state were  
10 calcined for 8 hours at 1000 °C and at 1200 °C. The calcined P-200 sample contained alpha-alumina after calcination at 1000 °C, whereas the calcined 5 wt% lanthanide-containing microcrystalline boehmite did not. When comparing the calcined lanthanide-containing quasi-crystalline boehmite with the lanthanide containing microcrystalline boehmite, it was clear that the MCB was  
15 thermally more stable than the QCB, because the calcined QCB was converted to alpha-alumina after calcination at 1200 °C with serious loss of surface area whereas the calcined MCB had not converted to alpha-alumina.

## Claims

- 5     1.    Micro-crystalline boehmite wherein an additive which improves the  
         MCB's suitability for use in catalytic or absorbent material is present in a  
         homogeneously dispersed state.
2.    Micro-crystalline boehmite according to claim 1 wherein the additive is a  
10       compound containing an element selected from the group of alkaline  
         earth metals, rare earth metals, alkaline metals, transition metals,  
         actinides, noble metals, silicon, boron, titanium, , and phosphorus.
3.    Process for the preparation of a micro-crystalline boehmite according to  
15       any one of the preceding claims wherein a micro-crystalline boehmite  
         precursor and an additive are converted to a micro-crystalline boehmite  
         containing an additive in a homogeneously dispersed state.
4.    Process according to claim 3 wherein more than one type of micro-  
20       crystalline boehmite precursor is used.
5.    Process according to claim 3 or 4 wherein aluminium alkoxide is  
         hydrolysed and hydrothermally aged to form micro-crystalline boehmite  
         containing additive.
- 25       6.    Process according to claim 3 or 4 wherein a soluble aluminium salt is  
         hydrolysed and precipitated as a hydroxide and hydrothermally aged to  
         form a micro-crystalline boehmite containing additive.

7. Process according to claim 3 or 4 wherein thermally treated aluminium trihydrate is rehydrated in water in the presence of an additive and aged at a temperature above 100 °C for a time sufficient to form micro-crystalline boehmite.
- 5
8. Process according to claim 3 or 4 wherein amorphous gel alumina is slurried in water in the presence of an additive and the resulting slurry is aged at a temperature above 100 °C for a time sufficient to form micro-crystalline boehmite.
- 10
9. Process according to claim 3 or 4 wherein quasi-crystalline boehmite is aged by (hydro)thermal treatment in the presence of an additive to form a micro-crystalline boehmite containing additive in a homogeneously dispersed state.
- 15
10. Process according to claim 3 or 4 wherein micro-crystalline boehmite is aged by (hydro)thermal treatment in the presence of an additive to form a micro-crystalline boehmite containing additive in a homogeneously dispersed state.
- 20
11. Process according to claim 3 or 4 wherein aluminium trihydrate is aged by hydrothermal treatment in the presence of an additive to form micro-crystalline boehmite.
- 25
12. Process according to any one of preceding claims 7-11 wherein the micro-crystalline boehmite precursor and the additive are shaped into a shaped body containing a quasi-crystalline boehmite precursor/additive mixture prior to the aging step.



13. Process according to any one of preceding claims 3-12 which is conducted in a continuous mode.
14. Process according to any one of preceding claims 3-13 wherein the reaction products are recycled to the reactor.
15. Process according to any one of preceding claims 3-14 wherein more than one aging step is used.
16. Shaped particle comprising a micro-crystalline boehmite according to any one of preceding claims 1-2.
17. Catalyst composition comprising micro-crystalline boehmite according to any one of preceding claims 1-2 and, optionally, binder material.
18. Transition alumina obtainable by thermal treatment of the micro-crystalline boehmite according to any one of preceding claims 1-2.
19. Transition alumina wherein additives are present in a homogeneously dispersed state, said additives being compounds containing elements selected from the group of alkaline earth metals, rare earth metals, transition metals, actinides, noble metals, silicon, boron, titanium, and phosphorus.
20. Catalyst composition comprising a transition alumina according to any one of claims 17-18 and, optionally, binder material.

Fig. 1 XRD of Catapal A

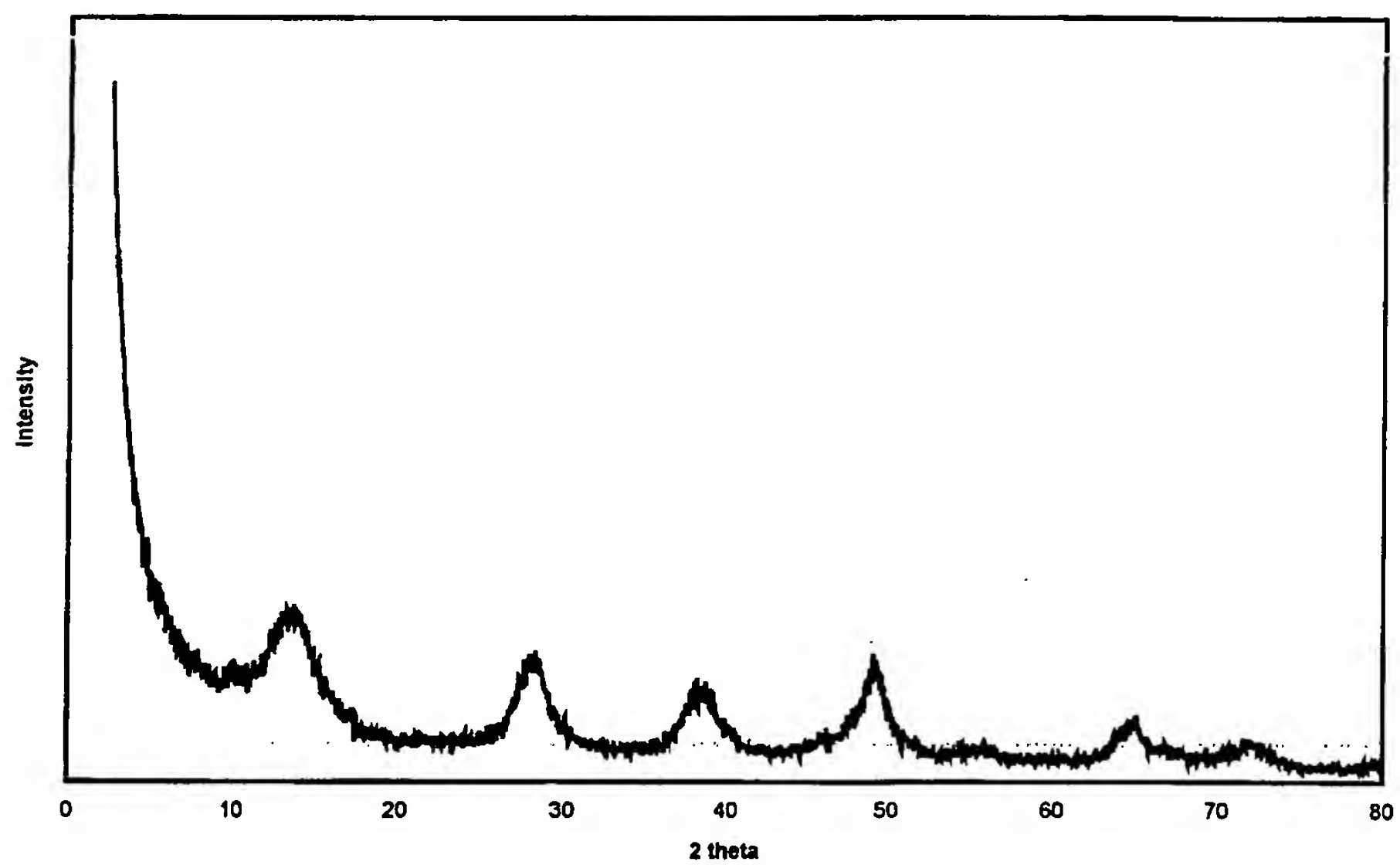


Fig. 2 XRD of P200

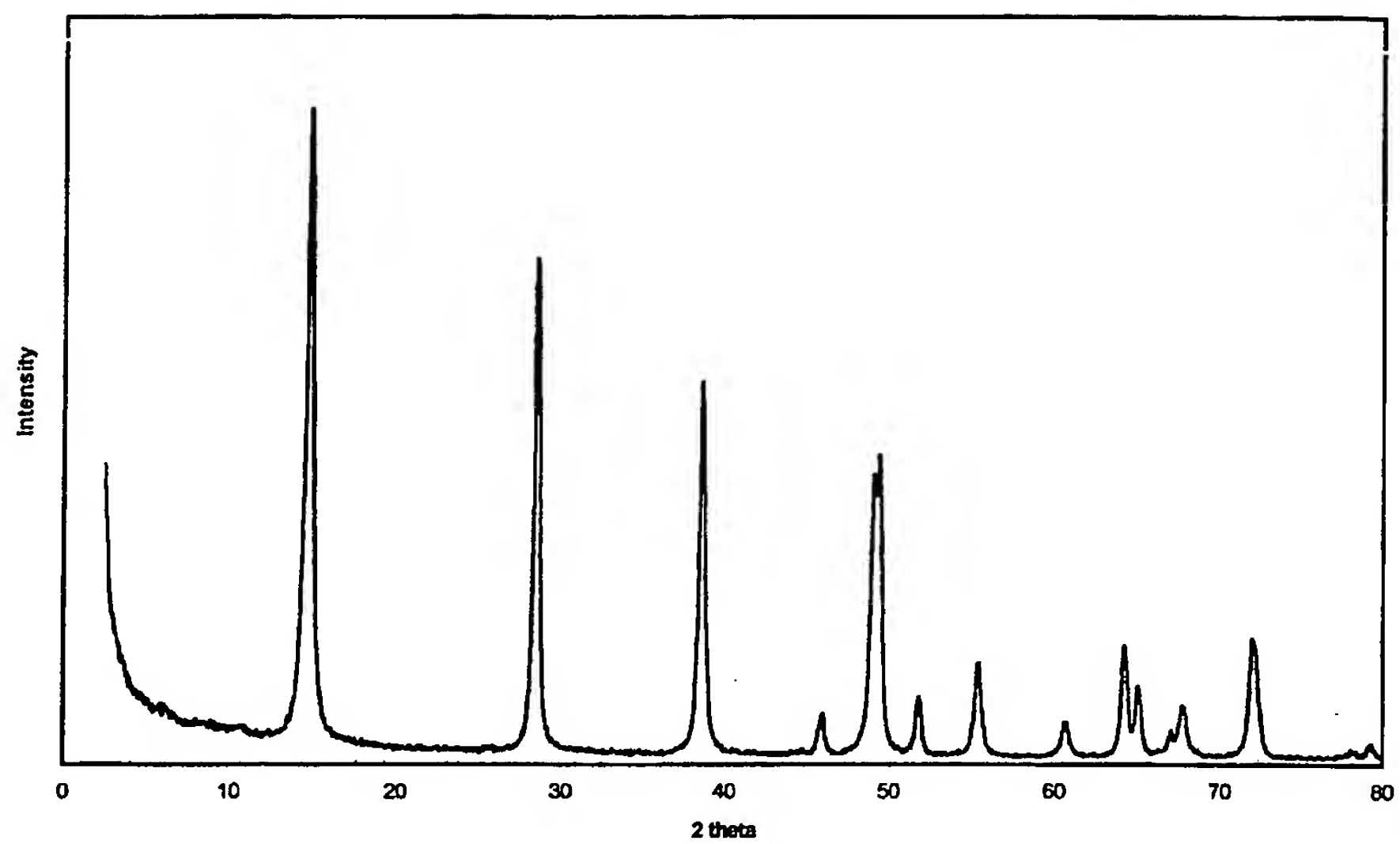


Fig. 3 MCB with 5wt% La

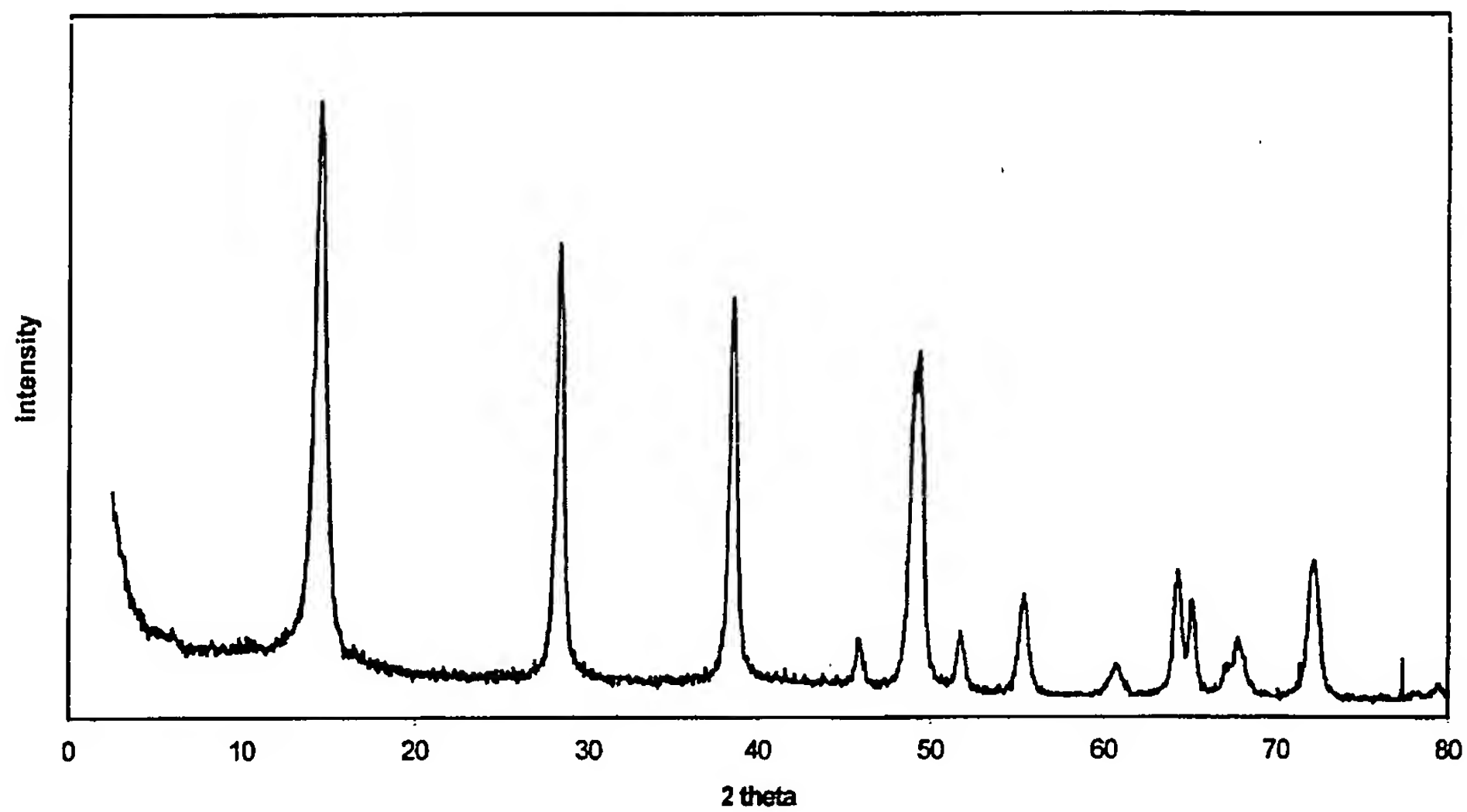


Fig. 4 MCB with 5wt% La from gibbsite

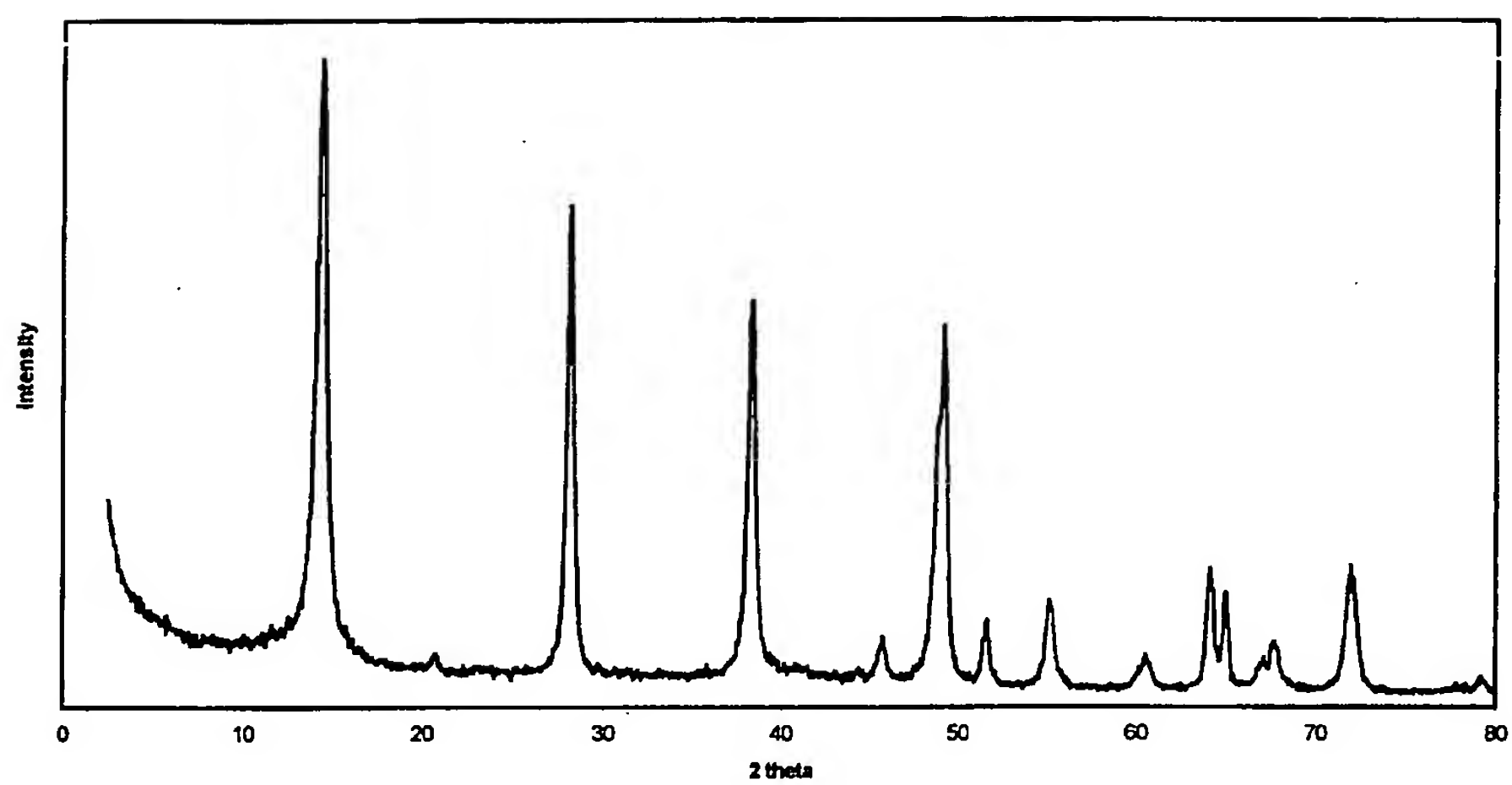


Fig. 5 MCB with 5 wt% La from CP alumina

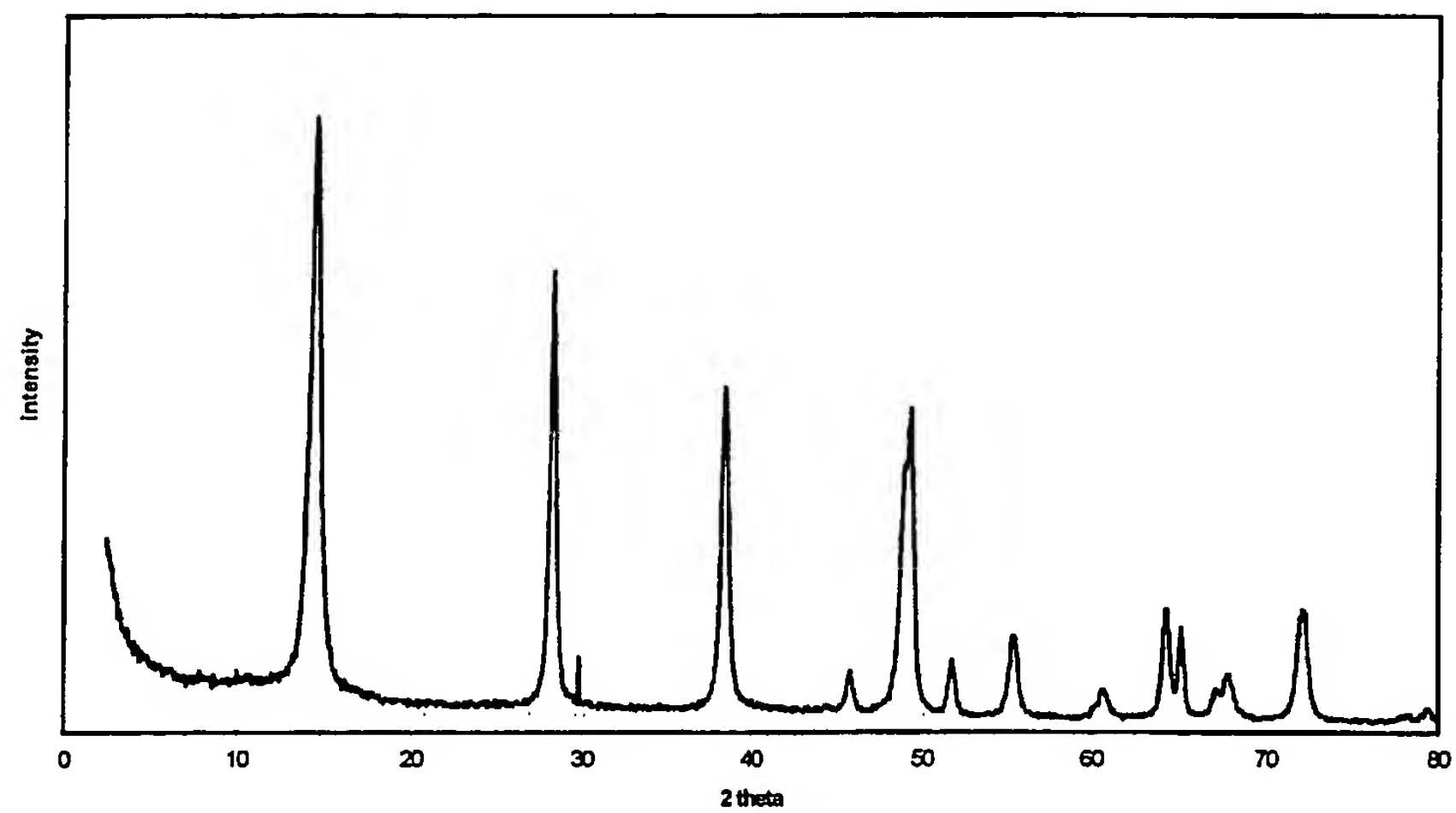


Fig. 6 MCB with 5 wt% La from Bayerite

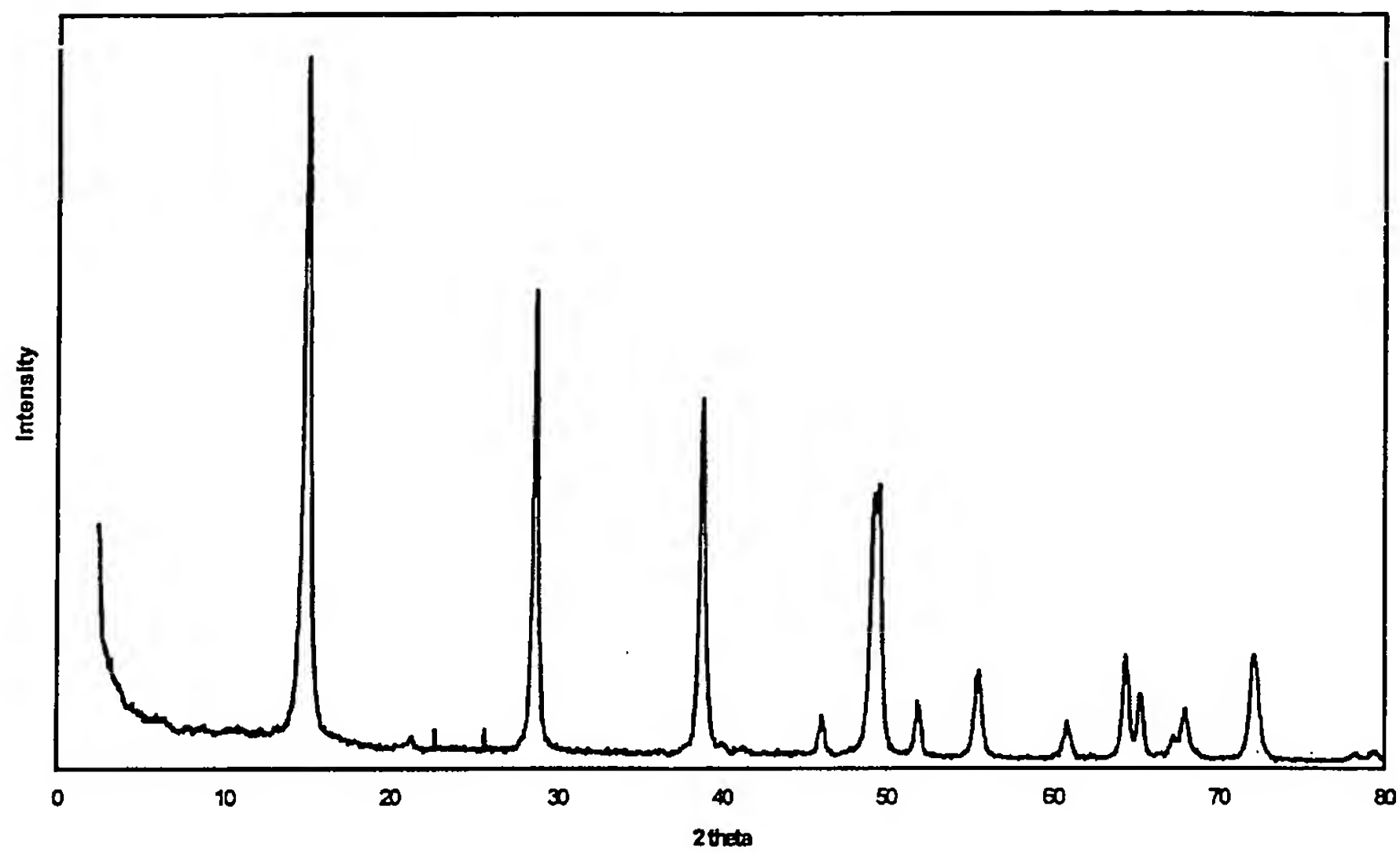




Fig. 7 MCB wit 5wt% La from gibbsite and Catapal

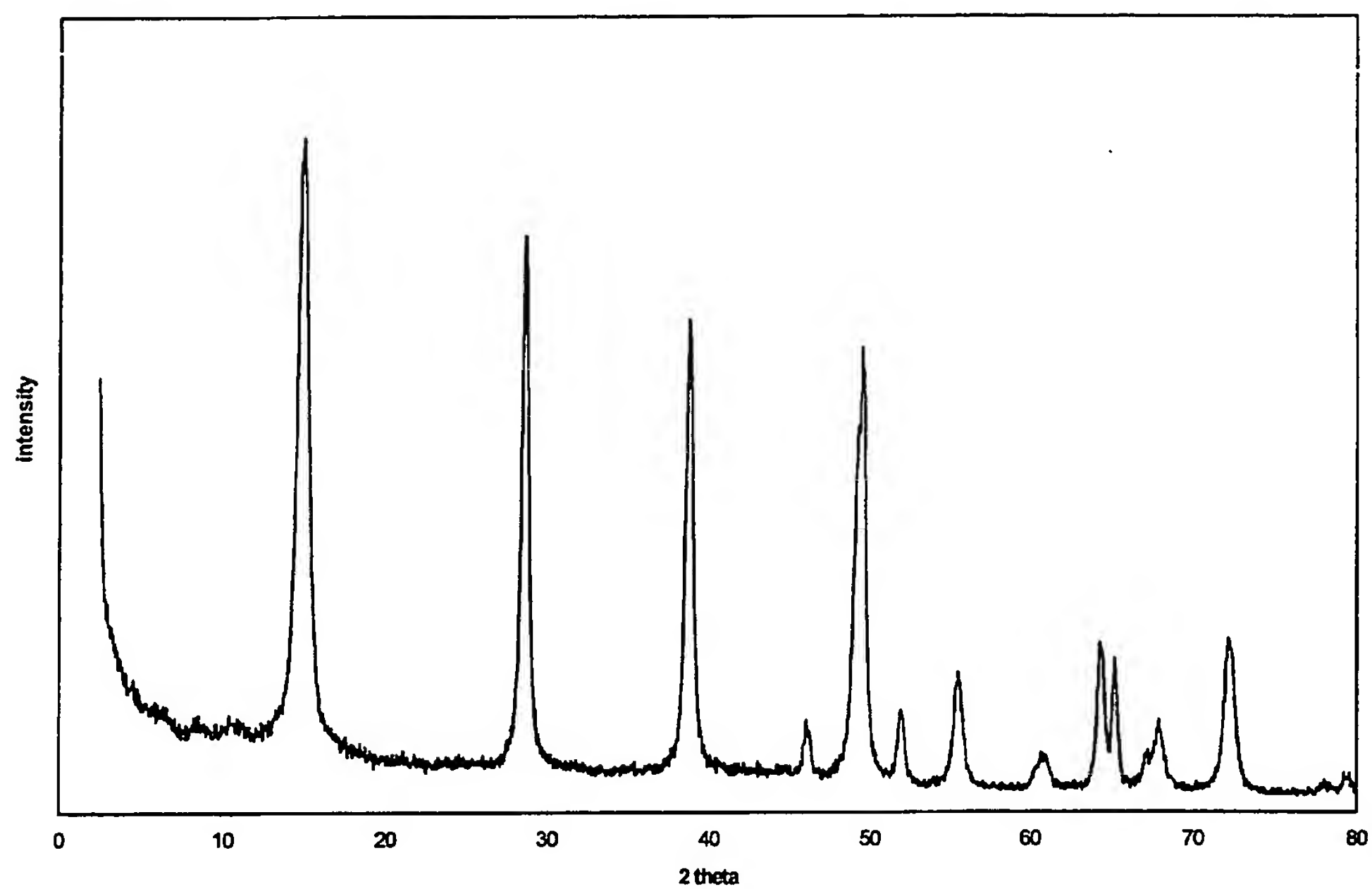


Fig. 8 MCB with 5wt% La from gibbsite and CP alumina

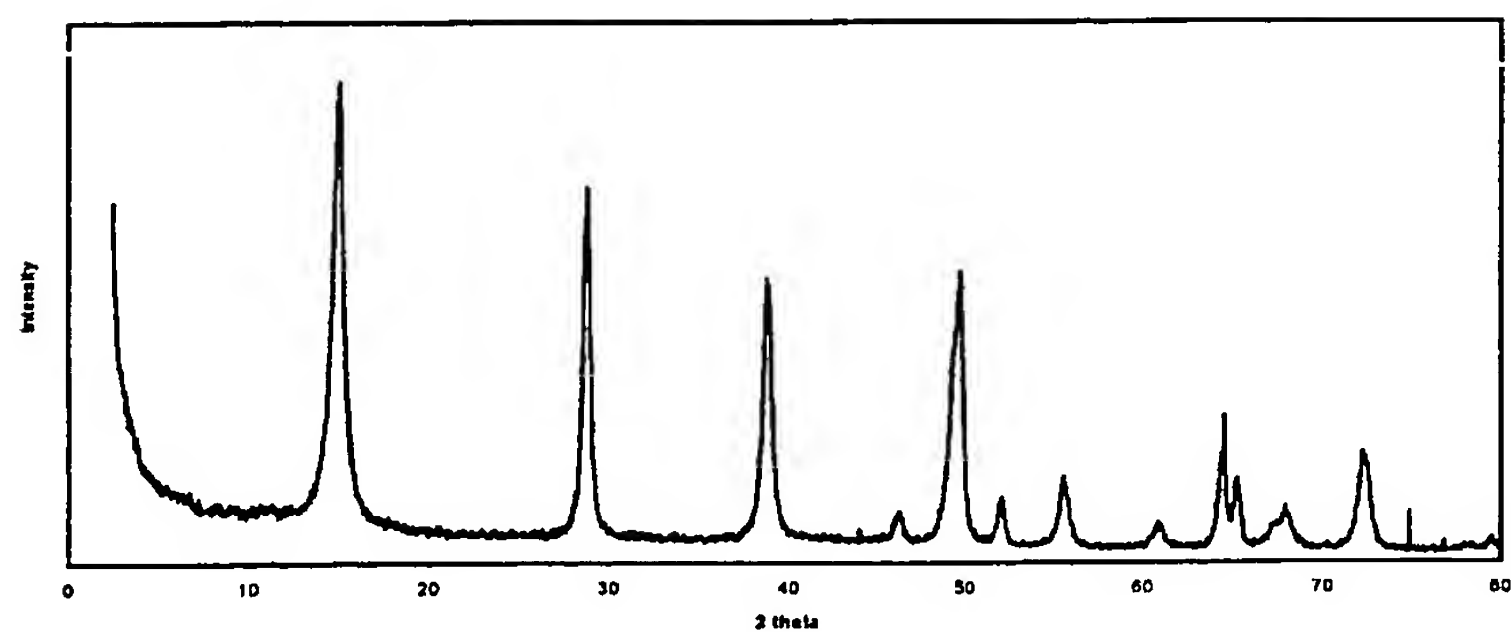
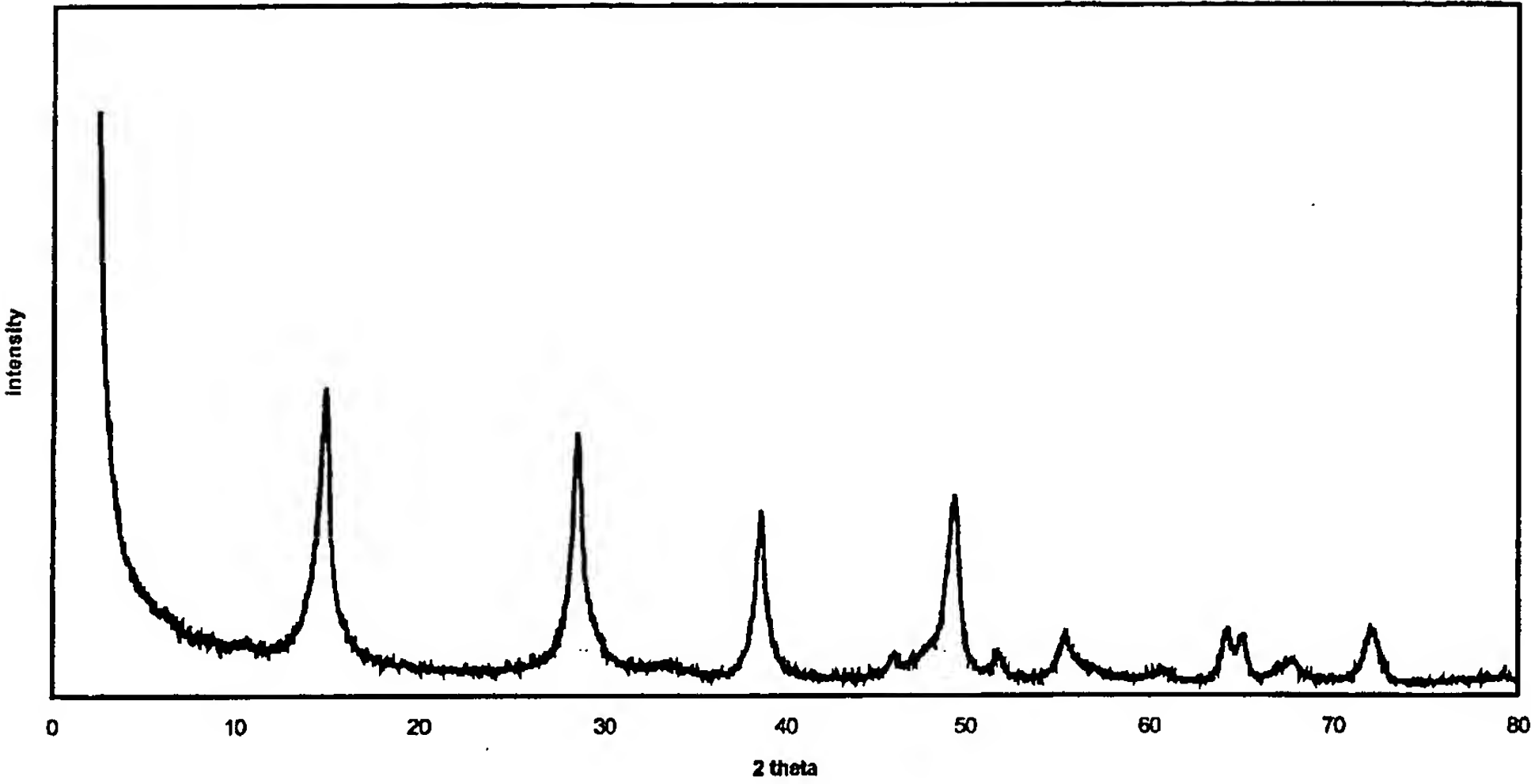
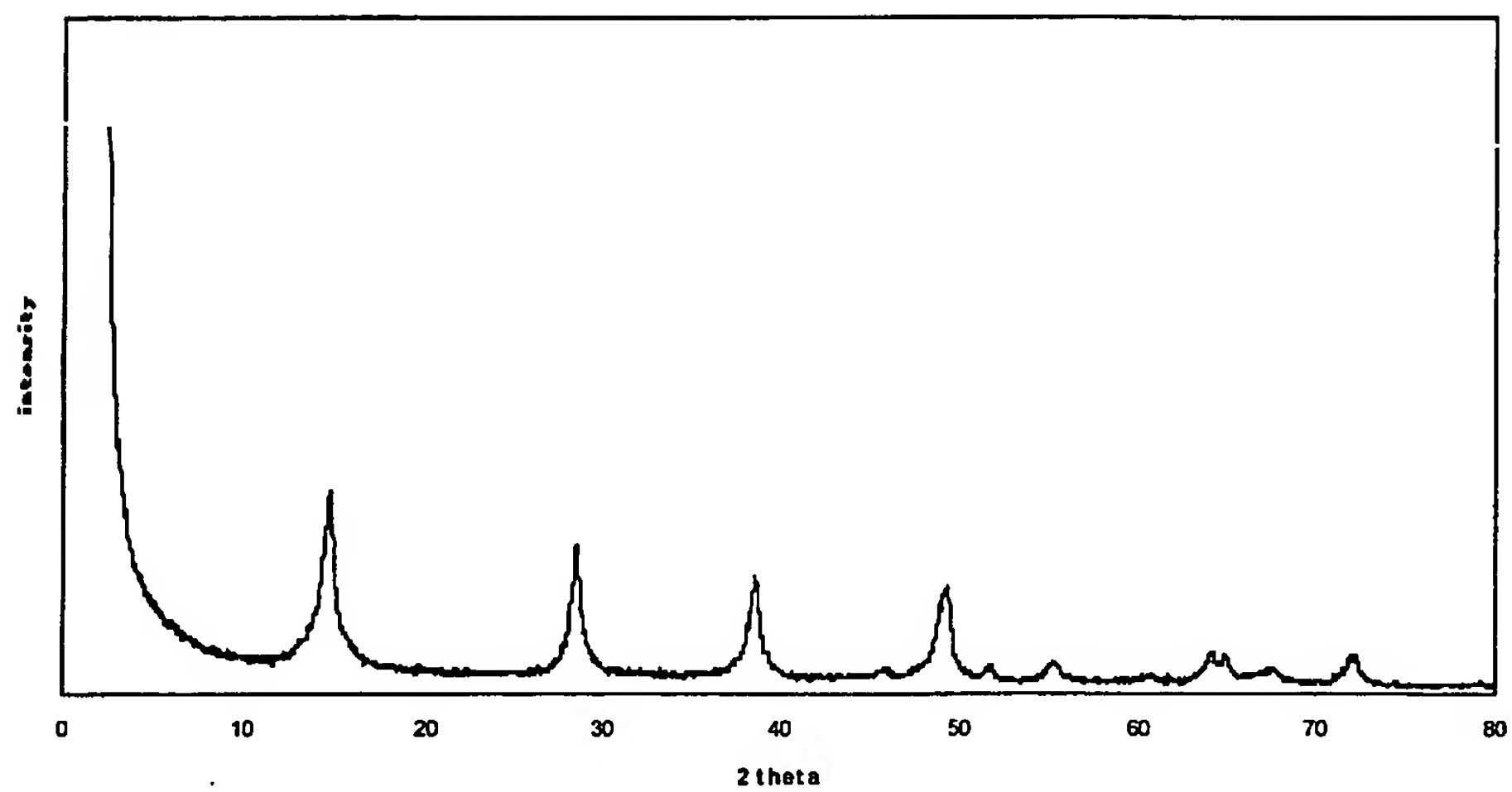


Fig. 9 MCB with 5wt% Ce from CP alumina



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Fig. 10 MCB with 5wt% Zn from CP alumina



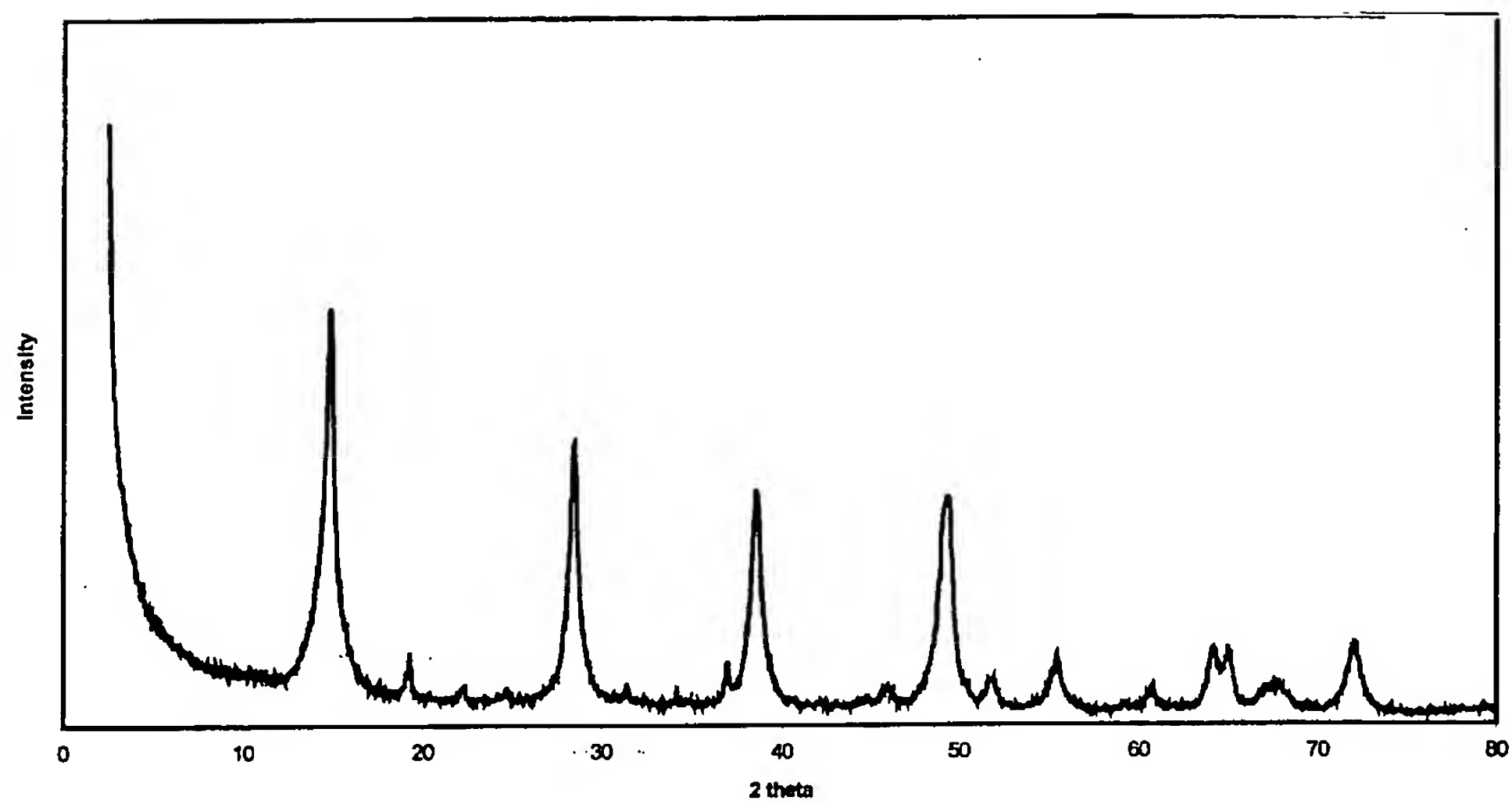
**Fig. 11** MCB with 5wt% Ba from CP alumina

Fig. 12 MCB with 5wt% La from BOC

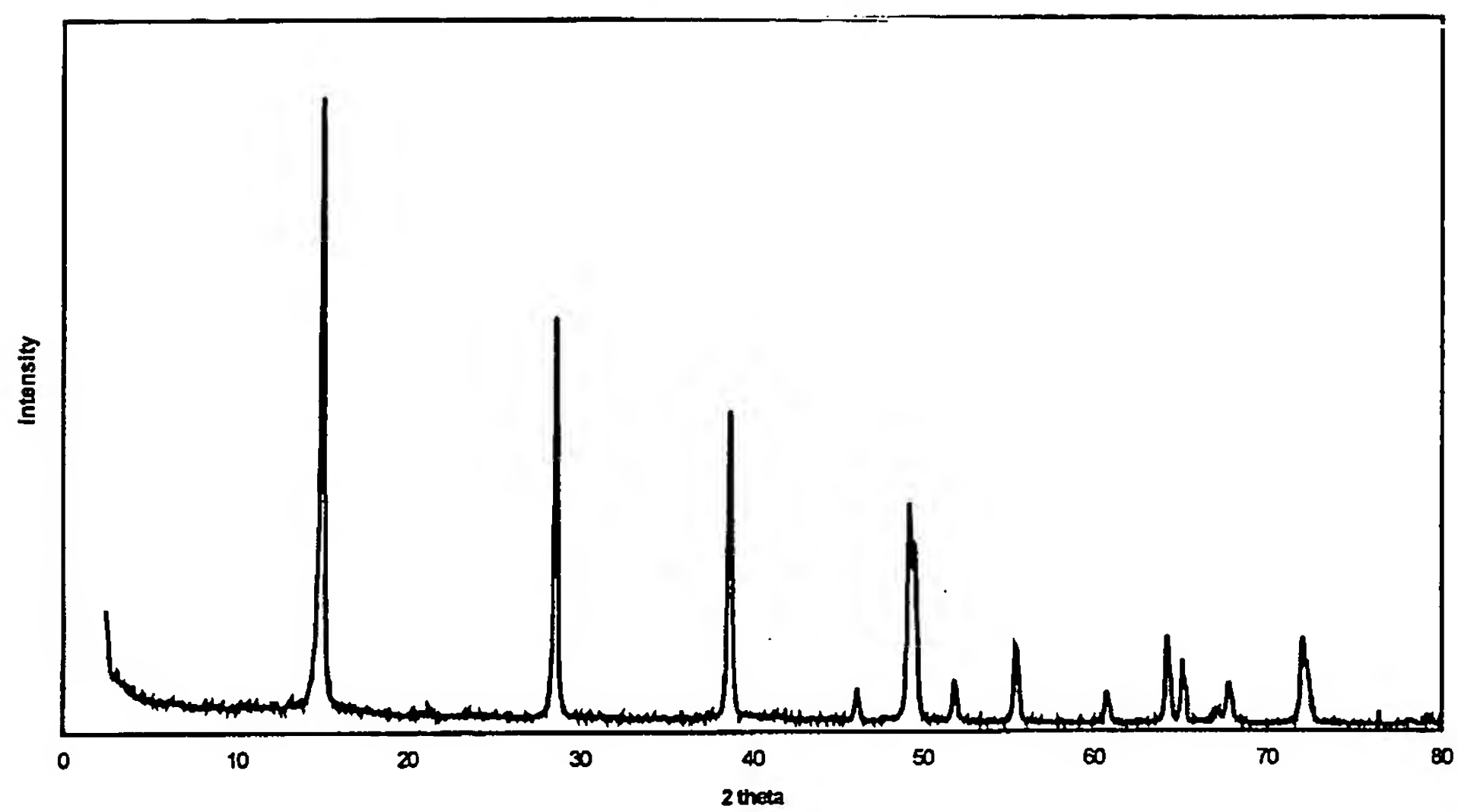


Fig. 13 MCB with 10wt% Ga from CP alumina

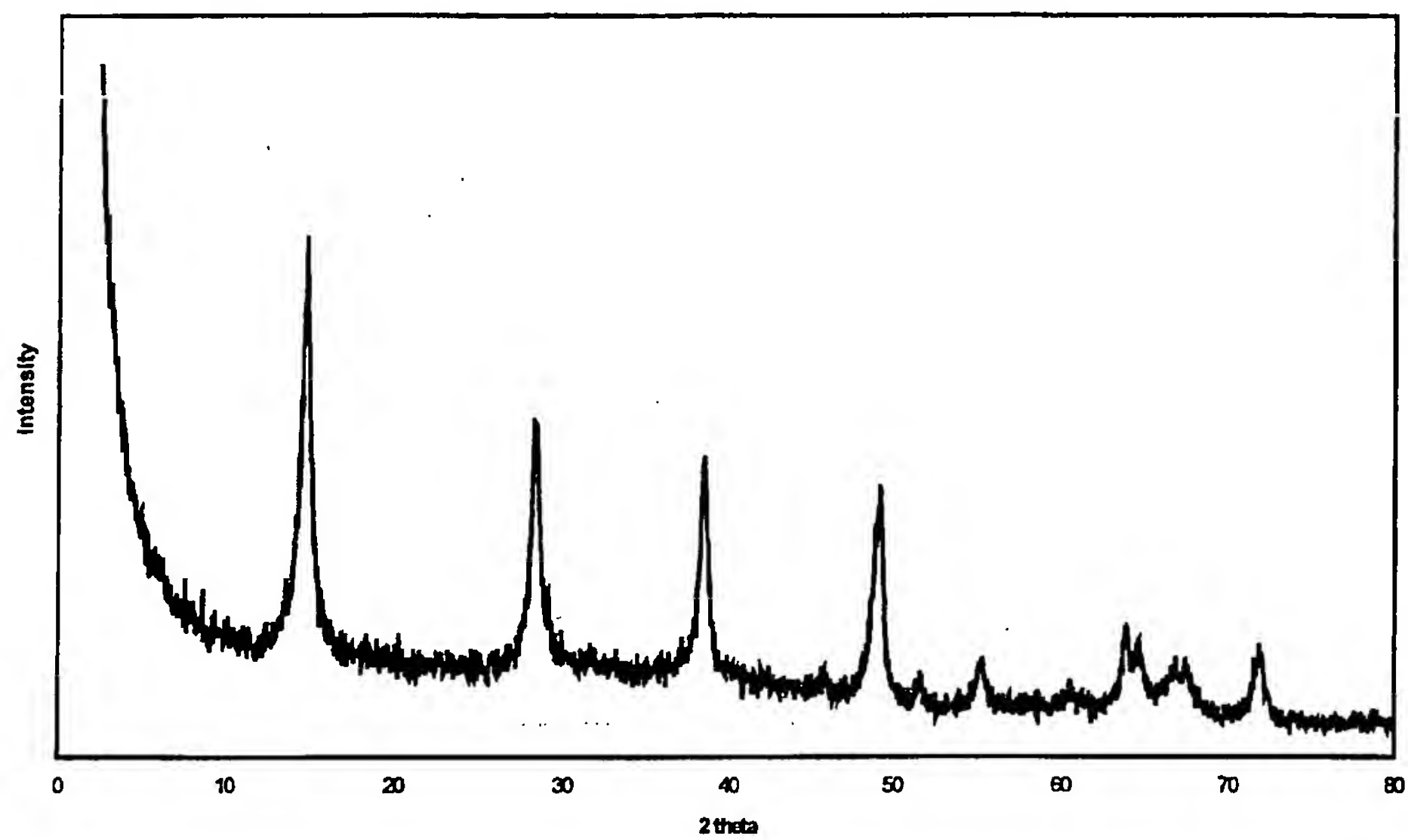




Fig. 14 MCB with 5wt% Si from CP alumina

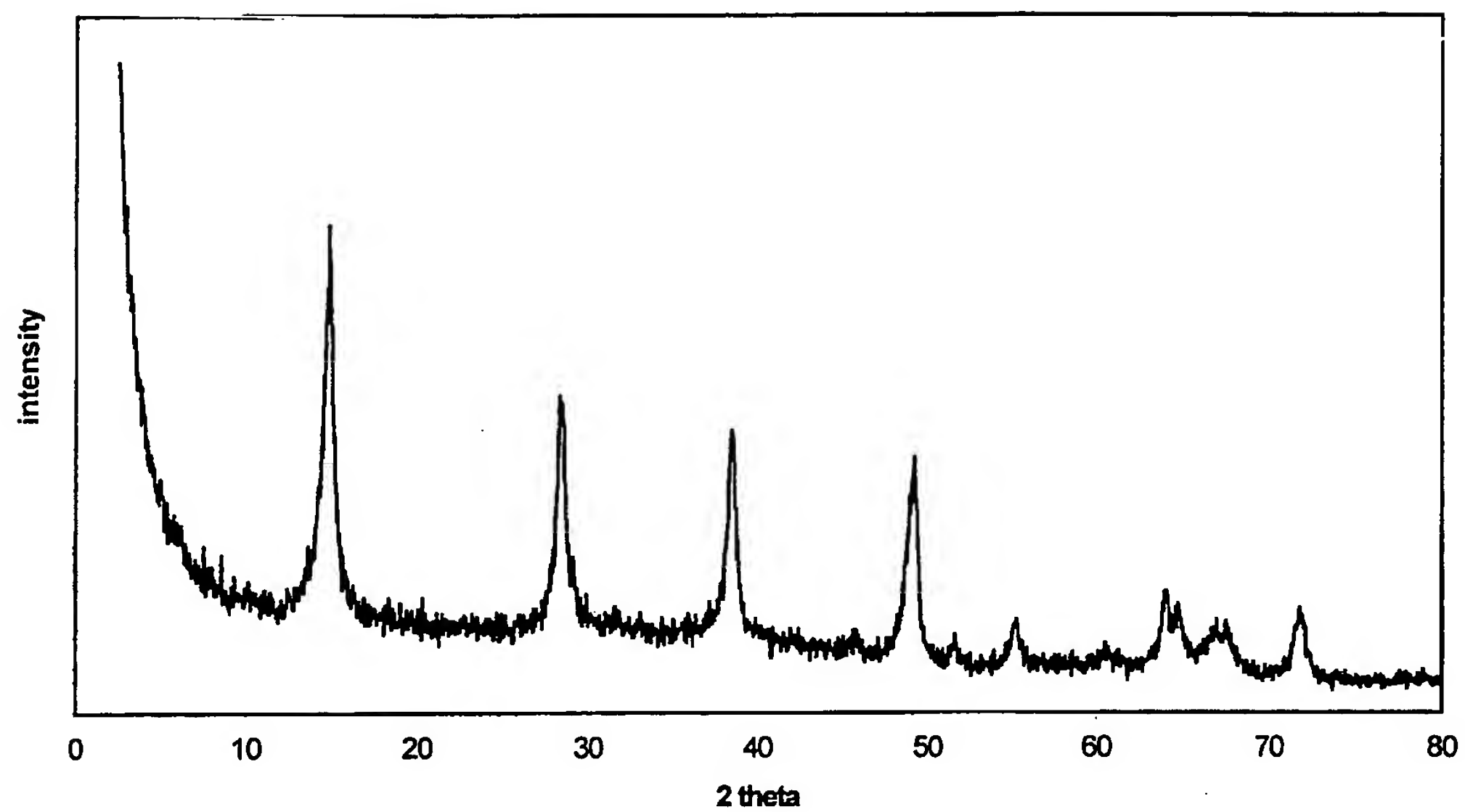
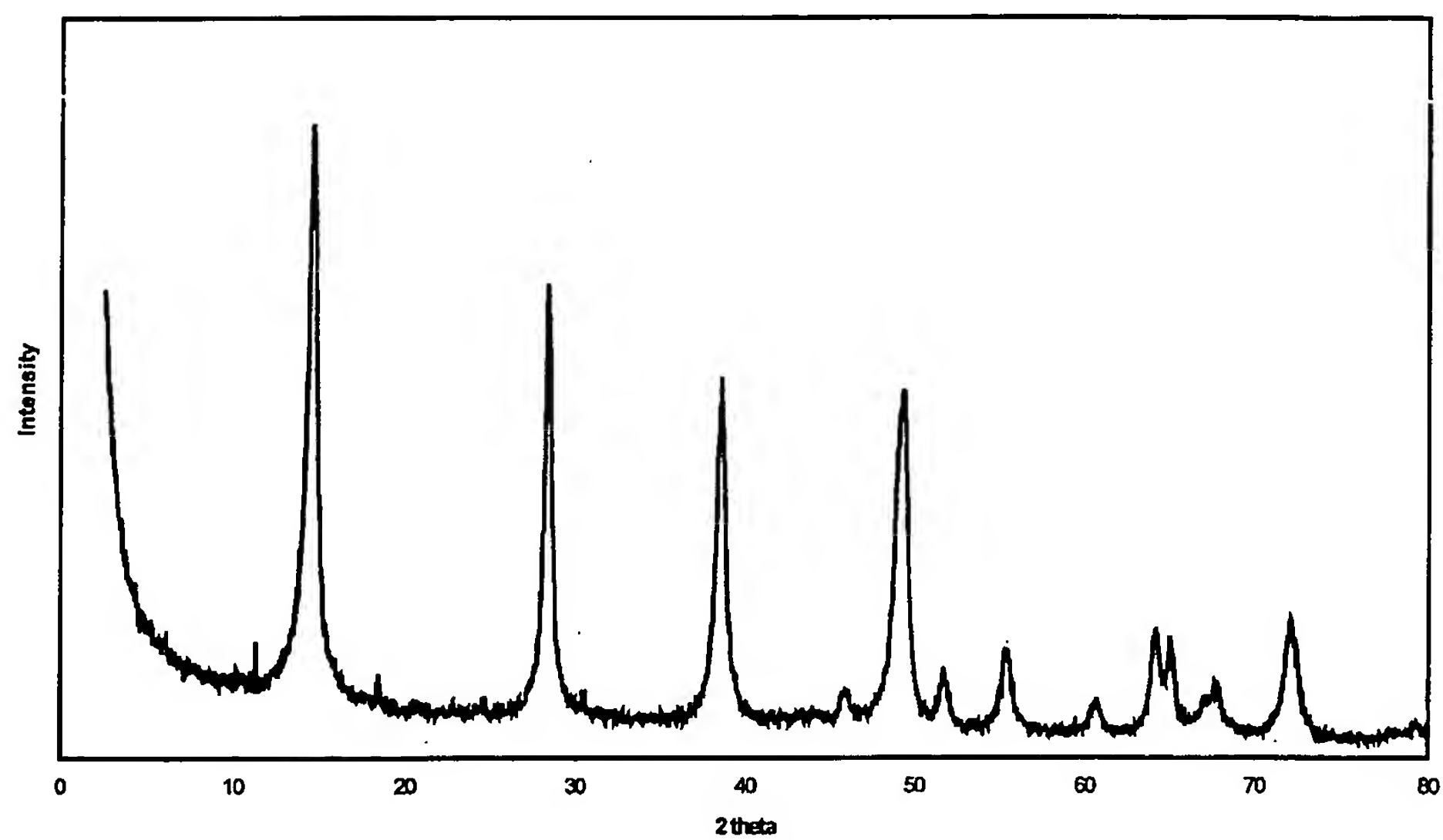


Fig. 15 MCB with 5wt% La from gibbsite and CP alumina



# INTERNATIONAL SEARCH REPORT

Int. .tional Application No

PCT/EP 00/07795

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C01F7/02 B01J20/08 B01J21/04 B01J35/10

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C01F B01J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

WPI Data, PAJ, EPO-Internal

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 304 721 A (NORTON CO) 1 March 1989 (1989-03-01) page 6, line 37 - line 49; claims ---	1-20
X	EP 0 597 738 A (RHONE POULENC CHIMIE) 18 May 1994 (1994-05-18) cited in the application column 5, line 30 - line 32; claims ---	18-20
A	---	1-17
A	US 3 357 791 A (D.R. NAPIER) 12 December 1967 (1967-12-12) cited in the application column 13, line 24 - line 35; claims --- -/--	1-20

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

21 December 2000

Date of mailing of the international search report

02/01/2001

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Zalm, W

INTERNATIONAL SEARCH REPORT

Int.      tional Application No PCT/EP 00/07795
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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WACHOWSKI L ET AL: "STUDIES OF PHYSICOCHEMICAL AND SURFACE PROPERTIES OF ALUMINA MODIFIED WITH RARE-EARTH OXIDES I. PREPARATION, STRUCTURE AND THERMAL STABILITY" MATERIALS CHEMISTRY AND PHYSICS, LAUSANNE, CH, vol. 37, 1994, pages 29-38, XP000956111 cited in the application page 30 -page 31 -----	
A	EP 0 505 896 A (NORTON CO) 30 September 1992 (1992-09-30) -----	

# INTERNATIONAL SEARCH REPORT

Information on patent family members

Int. l. Application No

PCT/EP 00/07795

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
EP 0304721	A	01-03-1989	US 4797139 A	10-01-1989
			AT 87277 T	15-04-1993
			AU 595463 B	29-03-1990
			AU 2045288 A	16-02-1989
			BR 8804056 A	02-05-1989
			CA 1302681 A	09-06-1992
			DE 3879584 A	29-04-1993
			DE 3879584 T	23-09-1993
			DK 447188 A	12-02-1989
			IN 170641 A	25-04-1992
			JP 1069511 A	15-03-1989
			JP 2030766 C	19-03-1996
			JP 7061861 B	05-07-1995
			KR 9602622 B	24-02-1996
			MX 164999 B	13-10-1992
			NO 176513 B	09-01-1995
			NZ 225586 A	26-07-1991
			ZA 8805490 A	26-04-1989
EP 0597738	A	18-05-1994	FR 2697832 A	13-05-1994
			AT 155766 T	15-08-1997
			BR 9304680 A	14-06-1994
			DE 69312426 D	04-09-1997
			DE 69312426 T	12-02-1998
			DK 597738 T	25-08-1997
			ES 2106302 T	01-11-1997
			FI 934986 A	13-05-1994
			GR 3024943 T	30-01-1998
			JP 2594879 B	26-03-1997
			JP 7309619 A	28-11-1995
			KR 9705530 B	17-04-1997
			MX 9306989 A	31-01-1995
			RU 2099135 C	20-12-1997
			US 5718879 A	17-02-1998
			ZA 9307855 A	19-05-1994
US 3357791	A	12-12-1967	NONE	
EP 0505896	A	30-09-1992	US 5178849 A	12-01-1993
			AU 641082 B	09-09-1993
			AU 1100292 A	28-01-1993
			BR 9200840 A	01-12-1992
			CA 2061112 A,C	23-09-1992
			DE 69214335 D	14-11-1996
			DE 69214335 T	24-04-1997
			JP 2886725 B	26-04-1999
			JP 5070121 A	23-03-1993
			MX 9201235 A	01-10-1992
			ZA 9201171 A	25-11-1992